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Synthesis and Characterisation of Inorganic Acid Doped Conducting Polymer

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Abstract

Conducting polymeric materials containing conjugated bonds have attracted much interest in scientific and technological areas in recent years. The unique optical, electrical and chemical properties offer these materials to be used in electronic displays, telecommunication, biosensors, anti-corrosion coatings and etc. On comparing with polyaniline, poly ortho toluidine have attracted considerable attention as they exhibit better solubility in wide range of solvents. Poly (o-toluidine) (POT) was synthesized by chemical oxidative polymerisation technique by using sulfuric acid (H_2SO_4) as protonisation agent and ammonium peroxo disulfate (APS) as oxidizing agent .The optical, structural, morphological and size of particles have been investigated. X-ray diffraction showed that the POT is a partially crystalline polymer due to doping of highly concentrated sulfuric acid. A flaky like feature was observed via scanning electron micrograph (SEM). Better protonation effect of POT was indicated by UV spectroscopy. Chemical structure of POT was investigated by FT-IR. Nano particle size analysis displays that the synthesized POT has good result because the particle size is below than 100 nm.

Keywords : *POT, FT-IR, optical and structural properties, SEM, Particle size.*

1. INTRODUCTION

Conducting polymer is also known as conjugated organic polymer with the highly π-conjugated polymeric chains. It has been widely used in different areas such as chemical and biosensors, catalyst, photovoltaic cells, batteries, supercapacitors and energy storage device applications and etc., due to its excellent unique optical properties and electrochemical activity and biocompatibility. A different kinds of conducting polymers have been developed for different applications (Duong Nguyen Nguyen and Hyeonseok Yoon, 2016).The properties of polymers obtained from substituted anilines is somewhat different fro those of polyaniline. Poly ortho toluidine (POT) is a derivative of polyaniline with methyl group (-CH_3) attached in the ortho position at the aromatic ring (Salma Bilal *et al.* 2014).

Chemical, electrochemical and photo-induced are the techniques to initiate the polymerization. In the first case, chemical oxidants such as ferric chloride, Ammonium peroxo disulfate (APS) are used to oxidize the monomer. In the second case the monomer is oxidized electrochemically and in the third technique a light is required to oxidize the monomer. Poor reproducibility of bulk conducting polymer and difficult to remove the grown film from the electrode surface are the drawbacks of electrochemical polymerization. Most of the conducting polymer in bulk form can be synthesized via chemical oxidative polymerisation which results in more homogeneous morphology than the electrochemical route (Babu *et al.* 2009; Sezer *et al.* 1999; Gorey *et al.* 2014).

In general conducting polymer exists in three different states classified as leucoemaraldine, pernigraniline, and emaraldine. Again it exists in two forms namely insulating and conducting state under the emaraldine form. The chemical route can generate nanosized particles of POT in the conducting state via optimizing the concentration of monomer and oxidizing

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agent. Notably, sulphuric acid (H_2SO_4) used as dopant (protonic acid) play a vital role in developing the properties of polymers. The partially crystalline conducting polymer can be achieved by doping of oxidizing agents and acids in the monomer solution.

Here we report a chemical oxidative polymerization pathway for the synthesis of nanosized and pure emaraldine salt form of POT. In the present work H_2SO_4 was used as a dopant, APS as an oxidant. After the end of the reaction, two phases are completely separated. The organic phase consist of POT- H_2SO_4 where as the aqueous phase consists of the reaction by products such as unreacted H_2SO_4 and APS. Very pure POT- H_2SO_4 in powder form can be seperated and washed several times with acetone to remove the impurities. After the seperation of POT- H_2SO_4 , the optical properties and particle size analysis of POT were found in Tetrahydrofuran (THF) as an organic solvent. With this improved physiochemical, optical and particle size distribution at nano range can lead to many exciting potential applications.

2. EXPERIMENTAL DETAILS`

2.1 Materials & Methods

O-toluidine (monomer, AR grade), sulphuric acid (H_2SO_4), ammonium peroxo disulfate (APS), Millipore water was used to prepare aqueous solutions.

The chemical oxidative polymerization of o-toluidine monomer was carried out at room temperature by the addition of 0.1 M of O-toluidine into 100 ml of aqueous solution which contain different molar concentration of H_2SO_4 with continuous stirrering for 45 minutes.0.1 M of APS which act as an initiator was dissolved in 25 ml of water and added drop wise into the polymerization bath. The polymerization solution was left for 5 h with continuous stirring. The supernatant was filtered and washed several times with millipore water followed by acetone to remove the excess of H_2SO_4 and APS. The sample was dried at 80° C in an oven until to be dry.

3. MATERIAL CHARACTERISATION

The x-ray diffraction studies of poly ortho toluidine were performed on XPERT diffractometer with Cu Kα X-ray λ=1.54 A°. The morphology of POT were observed by scanning electron microscopy (SEM).The Zeta sizer (Horiba, Japan) instrument is employed to find the size distribution of POT particles by dispersing the polymer in THF solvent with water. Optical properties of POT were characterized by UV-Visible spectrometer (DRS) - Analytekjena, Germany. IR spectra of POT were identified by using ATR-FTIR, Germany.

4. RESULTS & DISCUSSION

4.1 X-ray diffraction analysis

Fig.1 shows the XRD spectra of Poly ortho toluidine. Both crystalline and amorphous regions are exist in the POT spectrum in the range of 15-30°.XRD spectrum of polymer depends on the dopants and method used in synthesis. Many of the literatures reported that conducting polymers are amorphous in nature. It comes to crystalline nature when it is doped with strong protonic acids. Here sulphuric acid is a strong inorganic mineral acid which is used as protonic acid. It is very difficult to fix the conducting polymer in crystalline nature. Based on acid doping the state of polymer is partially crystalline in the range 22° due to the presence of rigid chain and ordered structure. Small peaks at 38°, 44°, 64° and 77° are also observed.

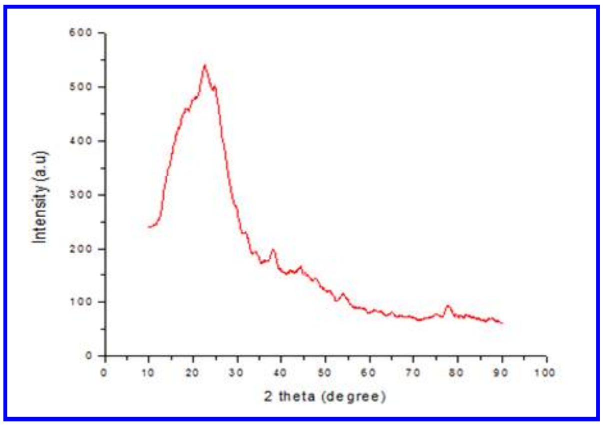

Fig. 1: XRD of POT – H_2SO_4

4.2 Morphological analysis

The surface morphology of immaculate POT were studied by SEM analysis. Fig.2 shows the uniform flaky like feature with few globular structures. The image discloses crystalline as well as amorphous regions. The crystalline region containing sharp edged particles and lamellar side were found to be interposed in the amorphous regions with particles of no well defined shapes. This morphological result is well matched with SEM results of highly crystalline and soluble DBSA doped Poly ortho toluidine (Sh M. Ebrahim *et al.* 2010).

4.3 Particle size analysis

During polymerization reaction a particle growth of polymer will happen. Initially, the solution

containing monomer is a clear liquid in which the size of the particles must be zero. But when the monomer is converted into polymer during the polymerisation reaction along with a propagation process that takes place. The growth of particle depends on reaction time. If the reaction time is increased long, polymer molecule chain will be formed. The dynamic light scattering mechanism is involved in measuring size of the particles. Fig.3 shows that the POT having particles with size 42.3 nm which is less than 100 nm is due to of proton molecule only react with reactive molecule of POT without any molecular formation.

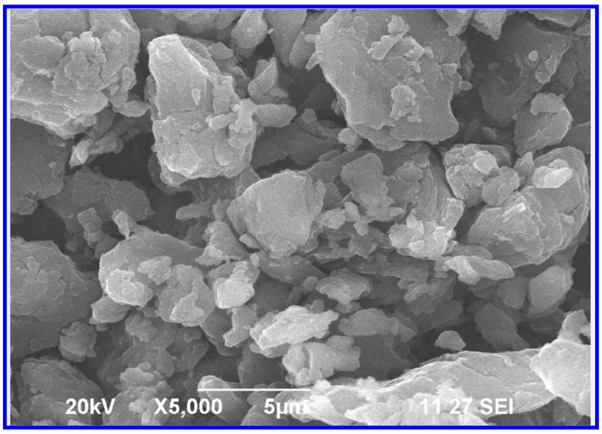

Fig. 2: SEM images of POT– H_2SO_4

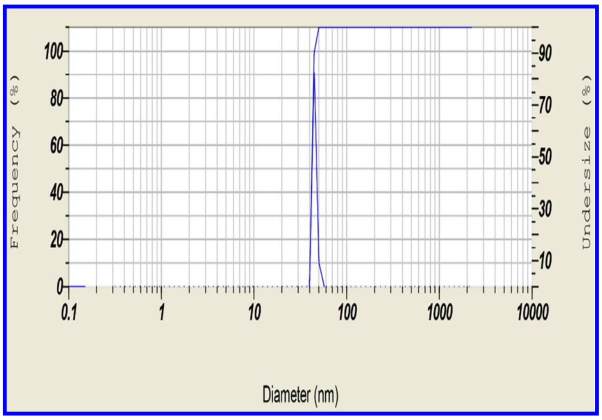

Fig. 3: Particle Size analysis by Zeta Sizer

4.4 UV-vis spectra analysis

The UV-vis spectra of H_2SO_4 doped POT as shown in fig.4. we notice that hypsochromic shift were observed at peak of 326 nm which correspons to π-π^*electronic transition of benzenoid rings and it represent the degree of conjugation between the adjacent benzenoid rings in the chain of polymer ((Salma Bilal *et al.* 2014). Instead of red shift in the absorption spectra of POT, we see that blue shift will be occur due to the steric effect of methyl group which reduces the degree of conjugation length in POT (Meixiang Wan and Jiping Yana, 1995). The absorption band located at 607 nm denotes the n- π^* transition of quinoid unit (Kakarla Raghava Reddy *et al.* 2008).The peaks at 759 and 855 nm are stronger and can be assigned to the emaraldine salt state of conducting polymer POT (Salma Bilal *et al.* 2014).

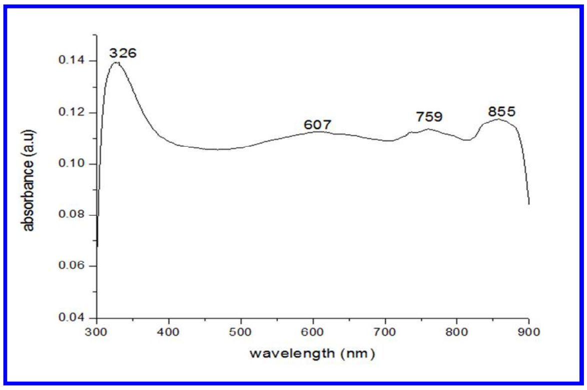

Fig. 4: UV-vis spectra of POT– H_2SO_4

4.5 FT-IR analysis

Fig.5 shows the FT-IR characteristic peaks of pure POT. The peaks at 1585 cm^{-1} and 1489 cm^{-1} has been assigned to C=C stretching of the quinoid and benzenoid rings. The peak at 1378 cm^{-1} can be attributed to the symmetric deformation of methyl group at ortho position .The peaks at 1206 cm^{-1} and 1152 cm^{-1} corresponding to C-C or C-N stretching and in plane C-H bending modes. The band at 1099 cm^{-1} indicates the charge delocalisation on the polymer backbone. The band at 1000 cm^{-1} and 934 cm^{-1} are assigned to C-H in plane bending vibration of quinoid rings. The band located at 796 cm^{-1} represents the out of plane bending vibration of C-H. These observed peaks are well matched with the literature reported earlier (Kakarla Raghava Reddy *et al.* 2008).

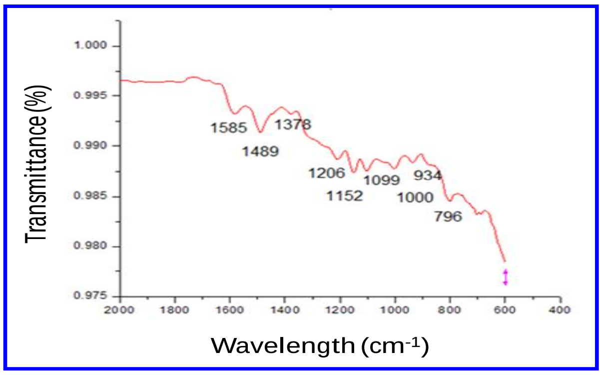

Fig. 5: FT-IR of POT– H_2SO_4

5. CONCLUSION

Zeta sizer was used to measure the particle size distribution of POT salts. The protonated POT salts were synthesized by chemical oxidative polymerization. SEM micrograph reveals that all the particles of POT are flakes with few globular structures. The properties such as surface area, reactivity, dissolution and stability in suspension may enhanced due to the nano size of particles of POT applicable for variety of potential applications such as catalyst and paint etc.

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